

# PATENT SPECIFICATION

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## (54) METHOD FOR SEPARATING A MIXTURE ACCORDING TO THE SPECIFIC GRAVITIES OF ITS CONSTITUENTS

(71) We, MITSUI MINING & SMELTING CO. LTD a Japanese Company of No. 1—1 Muromachi 2-Chome, Nihonbashi, Chuo-ku, Tokyo, Japan, do hereby declare this invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of separating a mixture of plastics according to the specific gravities of its constituents.

The quantities of plastics in industrial wastes and household wastes have been increasing in recent years, but no effective method for specific gravity separation of waste plastics has yet been established.

Plastics have a specific gravity of about 0.9 to about 1.4, and if floating method of separation is practiced by utilizing differences to specific gravity, the plastics mixture can theoretically be separated into groups which each have a similar specific gravity. Generally, however, plastics are hydrophobic, and can be wetted with water only with difficulty. When such plastics are put into water, small bubbles adhere thereto and, therefore, those plastics which have a high specific gravity and are settled below the water rise and mingle with the floating plastics due to the buoyancy of the bubbles, which results in a decrease in the accuracy of the separation. Furthermore, in the case of film-like plastics, plastics having a low specific gravity and plastics having a high specific gravity are intermingled due to the bubbles, and cannot be separated well.

Hence, in an attempt to change the surface hydrophobicity of plastics to surface hydrophilicity, there has previously been proposed applying a wetting agent in water or in solution, which procedure tends to give substantially the same hydrophilicity to all the plastics in the mixture.

It is an object of this invention to provide an effective method for the specific gravity separation of plastics mixtures.

In pursuit of the above object, it has been found that a more effective separation can be performed when plastics having a higher specific gravity are rendered selectively more hydrophilic than plastics having a lower specific gravity.

Accordingly, the present invention resides in a method of separating a mixture of plastics from one another in water or in an aqueous solution according to their respective specific gravities, the plastics having a minimum specific gravity difference of 0.01, the method comprising the steps of adding to said water or said aqueous solution a wetting agent selected from sodium ligninsulfonate, calcium ligninsulfonate, tannic acid, quebracho and gelatin so as to selectively render the more hydrophilic those plastics in the mixture which have the higher specific gravity, and then allowing the plastics of higher specific gravity to sink and the plastics of lower specific gravity to float.

The accompanying drawing is a graph showing the contact angles of various plastics with respect to a water droplet after being contacted with aqueous solutions containing varying concentrations of a wetting agent comprising equal amounts of sodium ligninsulfonate and tannic acid.

Referring to the drawing, the results shown in the graph were obtained by immersing the various plastics in wetting agent solutions of varying concentrations, drying them in air, then placing a drop of pure water or a solution on the surface of each plastic, and measuring the contact angle  $\theta$  of the water droplet using a contact angle measuring device of the goniometer type. The wetting agent used was a mixture of equal weights of sodium ligninsulfonate and tannic acid, while the plastics specimens investigated were polypropylene (specific gravity 0.90 to 0.91), polyethylene (specific gravity 0.94 to 0.97), polystyrene (specific gravity 0.98 to 1.10), and a polyvinyl chloride resin (specific gravity 1.35 to 1.45).

- As can be seen from the drawing, polypropylene is least affected by the concentration of the wetting agent, and the influence of the concentration of the wetting agent becomes progressively greater in the order of polyethylene, polystyrene, and polyvinyl chloride resin. Hence, the equal mixture of sodium ligninsulfonate and tannic acid has selective wettability according to the type of plastic involved and gives selective hydrophilicity to plastics having a higher specific gravity. Such a phenomenon is considered to be due to a selective adsorption of the wetting agent to the plastics surface.
- In addition to the above, other plastics suitable for use in the method of the invention are nylons (specific gravity 1.09 to 1.14) such as nylon 6, nylon 6/6 and nylon 6/10, polyvinylidene chloride (specific gravity 1.7 to 1.8), and an acrylonitrile/styrene copolymer (specific gravity 1.16 to 1.18).
- It is however, to be appreciated that the method of the present invention is not limited to the above mentioned plastics, although of course, the greater the specific gravity difference between the plastics the "more efficient" can be considered the separation. Conversely, the lesser the specific gravity difference the "less efficient" can be considered the separation. At minimal specific gravity differences between the constituent plastics being separated, the specific gravity separation of the present invention takes long periods of time. On a commercial scale, accordingly, it is preferred that the plastics mixture to be separated have a specific gravity difference of 0.01 or greater between the constituent plastics.
- In the present invention, the wetting agent used is selected from the group consisting of sodium ligninsulfonate, calcium ligninsulfonate, tannic acid, quebracho and gelatin. The concentration of the wetting agent in the liquid is more than about 0.5 ppm, preferably up to about 10 ppm. While greater amounts of wetting agent can be used, no commensurate increase in product efficiency is encountered and hence the use of such larger amounts of wetting agent is economically inadvisable. After adding the wetting agent, the water or solution is stirred for several minutes to allow the wetting agent to spread to every part of the plastics.
- Since the use of such a wetting agent as above at the time of separating a plastics mixture into constituents in water or in a solution according to their specific gravities results in rendering plastics having a higher specific gravity selectively more hydrophilic, such plastics sink and do not mix with the floating plastics, and a separation product having a high purity can be obtained.
- When in the method of this invention it is desired to separate a plastic having a specific gravity lower than 1 such as polypropylene or polyethylene from other plastics having a specific gravity higher than 1, the method can be performed in water.
- When in the method of this invention it is desired to separate polystyrene or an epoxy resin which has a specific gravity slightly higher than 1 from a polyvinyl chloride resin or acrylic resin having a higher specific gravity, the method is conveniently performed in an upwardly flowing stream of water or in a solution. The preferred flow rate of the plastics in the liquid varies in accordance with the shape and size of specimens and for example, in the case of a polystyrene pellet having a size of 2 mm in Example 2 of this specification the optimum flow rate was 3 cm/sec., whereas in the case of a polystyrene pellet having a size of 3 mm in the same Example, it was 5 cm/sec. While the flow rate of the plastics cannot be unequivocally defined, it can be easily established by one skilled in the art by a few small-scale process runs. Since the flow rate involved is primarily a function of the plastics size, the general approach is to start at a rather low flow rate, determine the acceptability of the results, and then increase the flow rate if the results are unsatisfactory. Usually, a few simple runs enables the optimum flow rate to be closely defined for any particular system.
- The solution used in sea water, brine, bittern containing water, or an aqueous solution containing halogen salts such as NaCl, MgCl<sub>2</sub> and MgBr<sub>2</sub>, sulfate salts such as MgSO<sub>4</sub>, CaSO<sub>4</sub>, K<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub>, or bicarbonate salts such as Ca(HCO<sub>3</sub>)<sub>2</sub> and NaHCO<sub>3</sub>.
- The method of the invention is applicable over a wide range of hydrogen ion concentrations, but it is preferred that the method is carried out at a pH range of about 5 to about 11, normally in a neutral region, from the standpoint of treating the waste water therefrom. Further, no problems are encountered even when the water contains inorganic materials such as silica, alumina, clay, and other inorganic minerals as well as certain organic substances such as fibrous materials and paper.
- There is no particular restriction on the shape and size of the plastics in the method of this invention, and when large quantities of plastics are to be treated, a suitable size for the plastics is not more than about 50 mm, preferably 1 to 40 mm.
- In the process of this invention, the

pressure utilized is generally atmospheric pressure, and the temperature utilized is generally room temperature (e.g., about 20 to 30°C). If the temperature is increased, a better effect can be expected but such is not suitable from an economical standpoint in that the additional capital cost and operating cost for the heating equipment is not accompanied by a commensurate benefit in process efficiency. The time of stirring is generally more than about 1 minute, and the time of standing is normally about 1 minute. (The time of standing can be determined in the case of stationary water (e.g. Example 1), but of course cannot be measured in the case of continuous processing (e.g. Example 2). However, these factors are not critical since the system is generally stirred for a sufficient amount of time to permit adequate contact between the wetting agent and the constituent plastics, and standing (when such is utilized) is merely allowed to proceed for a sufficient time to permit the plastics to float and sink, depending upon their specific gravities. As will be appreciated, these two factors cannot be unequivocally set forth since they will vary depending upon the exact system under consideration. They can, however, be easily determined by one skilled in the art by a few small scale process runs.

The following Examples illustrate the present invention in more detail and in each case all the processing was carried out at atmospheric pressure and at room temperature.

#### EXAMPLE 1

200 g of a mixture (pulverized to a size of 5 to 10 mm) consisting of 40 parts by weight of 0.4 mm thick film-like polypropylene (specific gravity 0.90) and 60 parts by weight of 0.4 mm thick film-like nylon 6 (specific gravity of 1.14) was placed in 20 l of water, and well mixed with stirring for 2 minutes, followed by standing for 1 minute. The polypropylene and nylon were of different colours so that the state of separation could be observed. Since the specific gravity of nylon 6 is greater than that of polypropylene, nylon 6 should sink in stationary water. However, following the above mixing, small bubbles adhered to the nylon, and 17% by weight of the nylon was found to come afloat because of the buoyancy of the bubbles.

When 100 g of sodium ligninsulfonate, per ton of the plastics mixture (the term "plastic mixture", of course, refers to the plastics per se), was added to the above plastics mixture in water, and the mixture in water stirred for 2 minutes and allowed to

stand for 1 minute, the polypropylene as floating material could be completely separated from nylon 6 as sinking material.

#### EXAMPLE 2

20 g of a mixture (pulverized to a size of 1 to 3 mm) consisting of 20 parts by weight of granular polystyrene (specific gravity 1.10), 30 parts by weight of granular nylon 6 (specific gravity 1.14) and 50 parts by weight of granular polyvinyl chloride resin (specific gravity 1.40) was charged in an elutriator containing 1,000 ml of water, and separation of the plastics was performed in an uprising stream of water. As in Example 1, the plastics had different colours. The elutriator has an inner diameter of 50 mm and a height of 300 mm. Water was supplied from the bottom of the elutriator while adjusting the flow rate of the polystyrene to 5 cm/sec for the 3mm polystyrene pellets, and the separation was performed in an uprising stream of water for 3 minutes. Since the polyvinyl chloride resin has the highest specific gravity among the three plastics, it should sink to the bottom of the elutriator. However, following the above mixing, small bubbles adhered to the plastics and 7.8% of the polyvinyl chloride resin was found to come afloat.

250 g of tannic acid per ton of the plastics mixture, was added to the plastics mixture. The mixture was well stirred, and fed into the elutriator followed by a separation in the same way as the above. As a result, air bubbles did not adhere to the polyvinyl chloride resin, and a mixture of polystyrene and nylon as an overflowing material was separated from the polyvinyl chloride resin as a sinking material. The recovery of the polyvinyl chloride resin was 98%.

#### EXAMPLE 3

Household waste plastics (pulverised to a size of 3 to 5 mm) were washed, and then placed in the same elutriator as was used in Example 2. These waste plastics were gathered from about 40,000 households in Funabashi-shi, Chiba, Japan, and contained polyolefins such as polypropylene (specific gravity 0.90 to 0.91) and polyethylene (specific gravity 0.94 to 0.97), polystyrene (specific gravity 0.98 to 1.10), polyvinyl chloride resin (specific gravity 1.35 to 1.45) and the like. When 50 g of the above material was directly charged into the elutriator containing 1,000 ml of water, small bubbles adhered to the polyvinyl chloride resin which was intended to sink, and the polyvinyl chloride resin floated. Thus, the separation efficiency was poor, and the recovery of the polyvinyl chloride resin was only 52.3%.

- 300 Grams, per ton of material, of quebracho as a wetting agent was added thereto, and the mixture well stirred. The mixture was then fed into the elutriator. As a result, bubbles did not adhere to the polyvinyl chloride resin, and the polyvinyl chloride resin could be recovered as sinking material at a ratio as high as 90.7%.
- The results of the separation by Examples of this invention and comparisons are shown in the following Table for this Example.

		Weight (%)	Cl Content (%)	Recovery (%)	Remarks
15	Starting Material	100.0	9.5	100.0	
	Floating Material	68.0	1.3	9.3	
	Sinking Material	32.0	27.0	90.7	Method of this invention
20	Starting Material	100.0	9.5	100.0	
	Floating Material	80.0	5.7	47.7	
	Sinking Material	20.0	25.0	52.3	Comparisons

#### EXAMPLE 4

- A mixture of 44 parts by weight of 0.4 mm thick film-like polypropylene (specific gravity 0.90) having a size of 5 to 10 mm, 16 parts by weight of polystyrene (specific gravity 1.10) having a similar size, and 40 parts by weight of a polyvinyl chloride resin (specific gravity 1.40) having a similar size was placed in stationary water so as to separate the constituents of the mixture. The separation was carried out the same way as Example 1, with the plastics again being of different colours. Part of the polystyrene and the polyvinyl chloride resin, which should have sunk in stationary water, floated as a result of the adhesion of small bubbles.

- Thus 2.6% of the polystyrene and 0.7% of the polyvinyl chloride resin floated in the floating material.

- 100 g of gelatin and 100 g of sodium ligninsulfonate, each per ton of the starting mixture, were added thereto, and the mixture well stirred and allowed to stand in water in the same manner as in Example 1. The purity of the polypropylene as a floating material increased up to 99.5%. When the material that sank in the above procedure was placed in an 8% aqueous solution of sodium chloride, polystyrene having a lower specific gravity than the solution was collected as floating material. The purity of the polystyrene collected was 99.5%.

- When a mixture of polystyrene and polyvinyl chloride resin, which sank when the above mixture of three kinds of plastics was subjected to floating separation without stirring with a wetting agent, was placed in an 8% aqueous solution of sodium chloride, the polyvinyl chloride resin mingled with the floating material, and the

purity of the floating polystyrene decreased to 87.5%.

#### EXAMPLE 5

A raw material mixture of empty receptacle scraps, 10 to 40 mm in size, consisting of 99 parts by weight of an acrylonitrile/styrene copolymer (specific gravity 1.16 to 1.18) and 1 part by weight of polyvinylidene chloride (specific gravity 1.7 to 1.8) was used for separation. The copolymer and polyvinylidene chloride polymer had different colours, so that the results of separation could be evaluated by the naked eye. The above mixture was fed into a specific gravity separation tank filled with a 25% aqueous solution of sodium chloride (the specific gravity of the solution was 1.19). As a result, the polyvinylidene chloride, having a higher specific gravity than the aqueous solution, floated onto the surface due to the adhesion of small bubbles, and mixed with the copolymer. The separation thereof was not good and 0.1% of the polyvinylidene chloride polymer in the floating material was found.

50 g of the mixture was placed in 1,000 ml of water, and 200 g, per ton of the material, of tannic acid as a wetting agent was added. The mixture was well stirred, and then fed into the above specific gravity separating tank. As a result, bubbles did not adhere to the polyvinylidene chloride polymer and the acrylonitrile/styrene polymer could be recovered as a floating material. The amount of the polyvinylidene chloride polymer in the floating material was less than 0.01%.

#### WHAT WE CLAIM IS:—

1. A method of separating a mixture of plastics from one another in water or in an

aqueous solution according to their respective specific gravities, the plastics having a minimum specific gravity difference of 0.01, the method comprising the steps of adding to said water or said aqueous solution of wetting agent selected from sodium ligninsulfonate, calcium ligninsulfonate, tannic acid, quebracho and gelatin so as to selectively render the more hydrophilic those plastics in the mixture which have the higher specific gravity, and then allowing the plastics of higher specific gravity to sink and the plastics of lower specific gravity to float.

2. A method as claimed in Claim 1, wherein the concentration of said wetting agent in water or in said aqueous solution is more than 0.5 ppm. 15

3. A method as claimed in Claim 1 or Claim 2, wherein the concentration of said wetting agent in water or said aqueous solution is less than about 10 ppm. 20

4. A method as claimed in Claim 1 of separating a mixture of plastics substantially as hereinbefore described. 25

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COMPLETE SPECIFICATION

1 SHEET

This drawing is a reproduction of  
the Original on a reduced scale

